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Jatropha curcas as a renewable source for bio-fuels—A review

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ABSTRACT

Fatty acid methyl ester derived from renewable lipid feedstock is popularly known as biodiesel, the substitute for petroleum based diesel fuel. The non-food oils such as Jatropha (*Jatropha curcas*), Karanja (*Pongamia pinnata*), waste cooking oil, by-product of vegetable oil refineries are the cheap feedstock for cost-effective production of biodiesel. Jatropha may be one of the most promoted oilseed crop throughout the world due to higher oil yield, suitable fatty acid composition of the oil, adaptability to diverse agro-climatic condition and low gestation period. The current article discusses the updated research and development initiatives undertaken for the study of chemical composition of Jatropha oil, techniques for synthesis of biodiesel using homogeneous catalyst, heterogeneous catalyst, enzymes (lipases) and non-catalytic supercritical process to obtain Jatropha based biodiesel satisfying ASTM 6751, EN 14214 and IS 15607 specifications.

Contents

1. Introduction

The increasing demand and price of crude petroleum as well as increasing level of green house gases in the atmosphere has driven the research interest for the development of alternative fuels from plant origin. Since the last two decades, bioethanol and biodiesel

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have gained the interest as alternative liquid fuels respectively to substitute gasoline and diesel. The current interest is to develop liquid fuel i.e. biodiesel for transportation and make it economically viable without affecting the food demand. The fuels derived from non-food sources are known as second generation biofuel. The second generation biofuel includes biodiesel from non-edible oil sources such as Jatropha (*Jatropha curcas*), Karanja (*Pongamia pinnata*), waste cooking oils, by-products of vegetable oil refineries, microalgal oil, etc. and ethanol from agricultural residues and wastes. Out of these, the non-edible oils obtained from seed bearing trees such as Jatropha and Karanja are the potential feedstock for biodiesel. Jatropha has been attracting the attention for its easy adaptability in tropical and subtropical climates in marginal and non-agricultural areas, although good environmental condition shows better crop performances and productivity. The hardy plant having rapid growth, ease of propagation and low gestation period are the advantages for selecting Jatropha as a source of vegetable oil feedstock for biodiesel. The Jatropha plant produces seed containing 27—40% non-edible oil [1], which can be converted to biodiesel to meet international biodiesel specifications. The current article focuses on the updated research and development undertaken on biodiesel production from Jatropha oil.

2. Properties of Jatropha oil for synthesis of biodiesel

2.1. Physico-chemical properties of Jatropha oil

The physico-chemical properties of Jatropha oil has been reported in the literature [2–7] and listed in Table 1. The free fatty acid (FFA, as oleic acid) of crude Jatropha oil ranges up to 15% [8], and sometimes up to 54% as reported by Payawan et al. [9], which are far beyond the limit of 1% maximum for the synthesis of biodiesel in laboratory scale using KOH or NaOH as catalyst. The limit of FFA is 0.1% maximum as specified by Lurgi and Desmet Ballestra for production of biodiesel in industrial scale to ensure the product to satisfy EN 14214, IS 15607 and ASTM 6751 specifications. Upon storage of Jatropha oil, the hydrolysis of triglyceride occurs as a result and the FFA increases fast [8]. The high FFA content Jatropha oil needs pretreatment steps for making it suitable for conventional alkali catalyzed transesterification for industrial scale biodiesel production. The iodine value and saponification value of oil are indicative of the structure of fatty acid such as the degree of unsaturation and chain length of fatty acid in triglyceride respectively. Both the iodine value and saponification value determine the cetane number of product biodiesel. The cetane index of product methyl ester is related to the iodine value and saponification value [10] as per Eq. (1), whereas cetane index is indicative of cetane number [11] as per Eq. (2). The average molecular weight MW_{Oil} of the oil can be calculated from the saponification value (SV) as per Eq. (3) [12], which is further used for stoichiometric calculation for transesterification reaction.

$$CI = 46.3 + \frac{5458}{SV} - 0.225 \times IV \quad (1)$$

$$\text{Cenate number} = \text{Cetane index} - 1.5 \text{ to } + 2.6 \quad (2)$$

$$MW_{Oil} = \frac{3 \times 56100}{SV} \quad (3)$$

2.2. Fatty acid composition of Jatropha oil

The fatty acid composition of an oil is one of the important characteristics apart from the chain length and degree of unsaturation which are indicative of the physical state of the oil and biodiesel, cetane number and also cold flow properties such as cloud point, pour point, cold filter plugging point (CFPP) and cold soak filtration test (CSFT) of biodiesel. The fatty acid composition of Jatropha oil has been reported in the literature [4–5,7,13–15] and summarized in Table 2. The unsaturated fatty acid in Jatropha oil ranges from 77% to 83%, and the cold flow properties of product biodiesel is dependent on the extent of unsaturation in the oil. Palmitic acid and stearic acid are the major saturated fatty acids in the oil. The variation in the percentage of fatty acid composition of Jatropha oil as listed in Table 2 is due to the diverse agro-climatic condition for Jatropha cultivation.

3. Production of biodiesel from Jatropha oil

The straight vegetable oils have been studied as fuel in compression-ignition engines. The poor performance of the fuel had been observed since the vegetable oils have high viscosity and low volatility. The fuel qualities of vegetable oils may be improved by various processes such as dilution, micro-emulsion, pyrolysis and transesterification. The process of transesterification of vegetable oil is widely adopted for converting it to fuel. Vegetable oils are transesterified with a short chain alcohol i.e. methanol to produce fatty acid alkyl ester in order to reduce the density and viscosity of the oil and improve other fuel qualities. The process of biodiesel synthesis is the chemical transesterification of triglycerides which also consists of esterification of free fatty acids present in the vegetable oil feedstock, and in general the overall process is known as alcoholysis. The stearic hindrance is limited in all molecules involved in the biodiesel synthesis, and the reaction mechanism may be classified as Su-AC-B (following A_N+D_N mechanism, also referred to as $B_{Ac}2$) [16]. The transesterification of vegetable oil with methanol is catalyzed either by an acid, alkali, enzyme or heterogeneous catalyst to give rise to fatty acid methyl ester (biodiesel) as the product and crude glycerol as a by-product. The factors affecting transesterification of vegetable oil are alcohol to oil molar ratio, catalyst type, reaction temperature, rate of mixing and purity of the reactants. The process is also uncatalyzed in supercritical fluid (SCF) mediums such as supercritical states of methanol or ethanol. The product of vegetable oil transesterification is allowed to stand, such that biodiesel forms the upper layer and crude glycerol as lower layer. Crude glycerol is separated either by gravity separation or by centrifuge. The upper biodiesel layer contains methanol, catalyst, traces of soap, glycerol and other impurities. The crude biodiesel is subjected to post-transesterification processes for removing the impurities, washing and drying to obtain the final biodiesel. Table 3 lists the fuel quality of biodiesel as specified by ASTM 6751, EN 14214 and IS

Table 1
Physico-chemical properties of Jatropha oil.

Sl. no.	Properties	Ref. [2]	Ref. [3]	Ref. [4]	Ref. [5]	Ref. [6]	Ref. [7]
1.	Free fatty acid (as oleic, %)	1.5–19	2.67	0.62	2.23	22.6	5.1–6.3
2.	Iodine value (gI_2/100 g)	93–107	96–105	102	103.62	100.1	103.6
3.	Saponification value (mgKOH/g)	188–196	196–200	197	193.55	208.27	193.0
4.	Unsaponifiable matter (%)	0.4–1.1	–	0.4	–	–	–

Table 2
Fatty acid composition of Jatropha oil.

Fatty acid	Ref. [13]	Ref. [4]		Ref. [14]		Ref. [15]	Ref. [5]	Ref. [7]
		Non-toxic	Toxic	Variety Caboverde	Variety Nicaragua			
Myristic acid ($C_{14:0}$)	0–0.1	0.2	0.1	0.1	0.1	n.d.	0.1	n.d.
Palmitic acid ($C_{16:0}$)	14.1–15.3	13.4	15.3	15.1	13.6	14.2	14.2	13.4
Palmitoleic acid ($C_{16:1}$)	0–1.3	0.8	0.9	0.9	0.8	1.4	0.7	0.3
Stearic acid ($C_{18:0}$)	3.7–9.8	6.4	6.6	7.1	7.4	6.9	7.0	5.8
Oleic acid ($C_{18:1}$)	34.3–45.8	36.5	41.0	44.7	34.3	43.1	44.7	40.9
Linoleic acid ($C_{18:2}$)	29.0–44.2	42.1	3.53	31.4	43.2	34.4	32.8	39.6
Linolenic acid ($C_{18:3}$)	0–0.3	0.2	0.3	0.2	0.2	n.d.	0.2	n.d.
Arachidic acid ($C_{20:0}$)	0–0.3	0.2	0.2	0.2	0.3	n.d.	0.2	n.d.
Eicosenoic acid ($C_{20:1}$)	n.d.	0.1	0.1	n.d.	n.d.	n.d.	n.d.	n.d.
Behenic acid ($C_{22:0}$)	0–0.2	tr	tr	0.2	n.d.	n.d.	n.d.	n.d.
Lignoceric acid ($C_{24:0}$)	n.d.	tr	0.1	n.d.	n.d.	n.d.	n.d.	n.d.
Others	n.d.	n.d.	n.d.	0.1	0.1	n.d.	n.d.	n.d.

Results are presented as percent values of corresponding fatty acids.

Table 3
Specification of biodiesel for US, European countries and India.

Sl. no.	Properties	EN 14214-2008	IS 15607-2005	ASTM D 6751-09
1.	Density @15 °C, kg/m^3	860–900	860–900	n.s.
2.	Kinematic viscosity at 40 °C, cSt	3.5–5.0	2.5–6.0	1.9–6.0
3.	Flash point, °C, *min*	101	120	93
4.	Sulfur, ppm, *max*	10	50	15
5.	Carbon residue, % by mass, *max*	0.3	0.05	0.05
6.	Sulfated ash, % by mass, *max*	0.02	0.02	0.02
7.	Water content, ppm, *max*	500	500	500
8.	Total contamination, ppm, *max*	24	24	n.s.
9.	Copper corrosion, 3 h at 50 °C, *max*	1	1	3
10.	Cetane number, *min*	51	51	47
11.	Acid value, mgKOH/g, *max*	0.5	0.5	0.5
12.	Methanol, % by mass, *max*	0.2	0.2	0.2
13.	Ester content, % by mass, *min*	96.5	96.5	n.s.
14.	Linolenic acid methyl ester, % by mass, *max*	12	n.s.	n.s.
15.	Polyunsaturated (≥ 4 double bonds) methyl esters, % mass, *max*	1	n.s.	n.s.
16.	Monoglyceride, % by mass, *max*	0.8	n.s.	n.s.
17.	Diglyceride, % by mass, *max*	0.2	n.s.	n.s.
18.	Triglyceride, % by mass, *max*	0.2	n.s.	n.s.
19.	Free glycerol, % by mass, *max*	0.02	0.02	0.02
20.	Total glycerol, % by mass, *max*	0.25	0.25	0.24
21.	Phosphorus, ppm, *max*	4	10	10
22.	Sodium and potassium, ppm, *max*	5	To report	5
23.	Calcium and magnesium, ppm, *max*	5	To report	5
24.	Iodine value, gI$_2$/100 g, *max*	120	To report	n.s.
25.	Oxidation stability at 110 °C, h, *min*	6	6	3
26.	Cloud point, °C	n.s.	n.s.	To report
27.	Distillation T90 AET, °C, *max*	n.s.	n.s.	360
28.	Cold soak filtration test, s, *max*	n.s.	n.s.	360 (and 200 for use in temperature below −12°C)

n.s: not specified.

15607. The following sections describe different types of process for biodiesel production from Jatropha oil, their advantages and limitations.

3.1. Research and development on selection of catalyst/process

3.1.1. Biodiesel production using homogeneous catalyst

Vegetable oils are converted to biodiesel by the use of homogeneous catalysts such as strong acids (sulfuric acid, hydrochloric acid) and alkali i.e. hydroxides and alkoxides of sodium and potassium. The acid catalysts are less sensitive to moisture and cause no soap formation. The acid catalyzed process requires high reaction temperature, long reaction time and on the other hand, liquid acids are highly corrosive to the reaction vessels and also major pollutant to the environment. Alkali catalysts are preferred over the acid catalysts since alkali are efficient to catalyze vegetable oil transesterification [17]. Alkali catalyzed transesterification proceeds 4000 times faster than that catalyzed by acid [18]. Homogeneous alkalis such as NaOH and KOH are used as catalysts for the preparation of biodiesel from vegetable oils having low free fatty acids. Foidl et al. [14] reported the method for preparation of methyl and ethyl esters from Jatropha oil using KOH as a catalyst in two steps. The process for preparation of biodiesel was also studied in a pilot scale which produced methyl esters with a purity of 99.5%. Sarin et al. [15] has studied the process by NaOH and KOH catalyzed transesterification of Jatropha oil in a single step process and determined the fuel quality of biodiesel blends from Jatropha and Palm oil. In another study Chitra et al. [19] optimized the experimental conditions for NaOH-catalyzed process. A methyl ester yield of 98% was achieved using 20% of methanol by weight of oil, and 1% NaOH as catalyst at a reaction temperature of 60 °C for 90 min. The scale-up of the process was studied in a 75 l capacity pilot plant which achieved 96% yield of biodiesel.

The synthesis of biodiesel from Jatropha oil containing high free fatty acids needs pretreatment steps. The pretreatment step reduces the level of FFA to make the product suitable for alkali transesterification. There are three types of pretreatment steps to reduce FFA in the feedstock namely, (1) esterification with glycerol/methanol (2) physical refining and (3) neutralization. Esterification of FFA with methanol or glycerol is conducted for the pretreatment of high FFA oils. The process of FFA esterification with methanol is catalyzed by an acid to produce methyl esters. There are little chances that the catalyst used during the process may contribute to the sulfur content of the product biodiesel. The esterification of FFA with glycerol gives rise to glyceride and water. The process may be uncatalyzed for the esterification of FFA with glycerol when the reaction is conducted at high temperature under vacuum so that water formed is removed from the reaction vessel shifting the equilibrium towards the formation of glycerides. In case of physical refining, the oil is treated with high temperature under vacuum so that the free fatty acid as well as volatile impurities is removed. The process is practised in the industrial scales where the free fatty acids are separated from the oil producing refined oil with acid value less than 0.2 mgKOH/g. The physical refining is often adopted for vegetable oil refineries where the FFAs and volatile impurities are removed with little loss of oil. Neutralization is performed where the feedstock does not contain considerably high amount of FFA. The oil is treated with an appropriate amount of alkali such as sodium hydroxide solution; the amount of sodium hydroxide is calculated from the acid value or FFA of the oil. During this process, FFA is converted to soap which is removed by water washing. The loss of oil during neutralization is high.

Esterification of high FFA oil with methanol to form methyl ester is the most preferred process of pretreatment as it is associated with no loss of materials. The process is catalyzed by acids such as sulfuric acid, sulfonic acid, hydrochloric acid and most commonly used is sulfuric acid. The low FFA oil after esterification is subjected to conventional alkali transesterification. Thus, the two step process i.e. acid catalyzed esterification followed by alkali-transesterification is adopted for biodiesel production from high FFA containing vegetable oils. The two step process for the synthesis of biodiesel from Jatropha oil containing 7% FFA was reported by Lu et al. [20], where the esterification process was catalyzed by 1% H_2SO_4 using 12% methanol in oil at a reaction temperature of 60 °C for 2 h. The acid value decreased from 14 mgKOH/g to below 1 mgKOH/g of oil. It has been observed that 90% of the phospholipids are removed during the acid catalyzed esterification process. The yield of biodiesel was more that 98% under the reaction conditions of methanol to oil molar ratio 6:1, catalyst concentration 1.3% KOH, temperature 64 °C for 20 min. Berchmans and Hirata [8] have reported the two step process to reduce the FFA of Jatropha oil from 15% to less than 1% by the process of esterification using 0.6 w/w methanol to oil ratio, 1% H_2SO_4 as a catalyst at reaction temperature of 50 °C for 1 h. The second step was transesterification of pretreated oil using 0.24 w/w methanol to oil ratio and 1.4% w/w NaOH to oil as alkali catalyst at a reaction temperature of 65 °C for 2 h; the final yield of biodiesel obtained was 90%.

Patil et al. [21] conducted the two step process for biodiesel production from Jatropha oil (containing 14% FFA) by acid esterification with 0.5% H_2SO_4, methanol to oil molar ratio 6:1, reaction temperature 45 ± 5 °C followed by alkali transesterification with 2% KOH, methanol to oil molar ratio 9:1 and reaction temperature 60 °C to achieve biodiesel yield of 90–95%. The same process is studied by Tiwari et al. [22] with Jatropha oil containing 14% FFA. The optimum conditions for esterification step is 1.43% v/v H_2SO_4 as acid catalyst, 0.28 v/v methanol to oil ratio and reaction temperature of 60 °C for 88 min to reduce the FFA to less than 1%. The second step KOH-catalyzed transesterification with optimal reaction conditions of 0.16 v/v methanol to pretreated oil ratio and reaction temperature of 60 °C for 24 min resulted above 99% yield of biodiesel with the fuel qualities satisfying the specified standards for biodiesel.

The ultrasonic assisted dual step process is a new approach for the synthesis of biodiesel from crude Jatropha oil with less reaction time and less energy input. The synthesis of biodiesel from crude Jatropha oil having acid value 10.54 mgKOH/g was conducted by the two step process i.e. acid catalyzed esterification followed by alkali-transesterification; both the stages were assisted by ultrasound [23]. It has been observed that after the first step pretreatment with H_2SO_4 for 1 h, the acid value decreased to 1.2 mgKOH/g. Then the second step NaOH catalyzed transesterification was conducted for 30 min to obtain 96.4% yield of biodiesel. The total reaction time needed is 1.5 h which is just half of the time taken for completion of conventional alcoholysis of oil.

The use of sulfuric acid for pretreatment step may cause sulfonation of the oil rich in unsaturated fatty acids and the traces of residual catalyst may result in the high sulfur content in biodiesel against the limit of 10 ppm maximum. Also the use of liquid acid is associated with environmental concerns. An eco-friendly approach is to conduct the esterification of FFA using solid acid catalysts under mild reaction conditions prior to alkali catalyzed transesterification. Lu et al. [20] reported the pretreatment of Jatropha oil containing different levels of free fatty acids, catalyzed by solid acids. The screening of solid acids for methanolysis of oleic acid revealed that SO_4^{2-}/TiO_2 is an active catalyst for esterification of free fatty acids. Under the reaction conditions of methanol to FFA molar ratio 20:1, catalyst concentration 4%, reaction temperature 90 °C for 2 h, the FFA conversion achieved was more than 97%. The pretreatment was followed by simple alkali-transesterification. Among the solid acid catalyst, SiO_2 treated with HF has higher number of Lewis acid sites effective for esterification of FFA present in crude Jatropha oil. Corro et al. [24] studied the pretreatment of crude Jatropha oil containing 18.05% FFA under the reaction conditions of methanol to crude Jatropha oil molar ratio 12:1, SiO_2•HF catalyst 10%, reaction temperature 60 °C for 2 h. The conversion of FFA achieved was 96% to obtain pretreated oil suitable for alkali transesterification. The stability of the solid acid catalyst was investigated. During 30 runs, the catalytic activity of SiO_2•HF towards FFA esterification remained unchanged, which indicates that the catalyst can be recovered and reused for the process. The approach of solid acid catalyzed pretreatment followed by alkali transesterification has the environmental benefits as well as the ease of attaining the required specification of product biodiesel.

3.1.2. *Biodiesel production using heterogeneous catalyst*

The conventional homogeneous process for biodiesel production needs separation and recovery of the alkali which is a major difficulty and needs dosing of equivalent amounts of acid i.e. HCl to neutralize the used catalyst. The aqueous quenching results in the formation of stable emulsion and causes difficulties for separation of methyl ester and glycerol. Also the process produces waste water which needs further treatment. Solid catalysts have the advantage that these catalysts can be easily recovered for reuse after completion of the reaction and eliminates the processing costs associated with that of homogeneous catalyst. The use of heterogeneous catalyst for biodiesel synthesis is an environmentally friendly process. Also the formation of soap in case of homogeneous alkali transesterification is eliminated by heterogeneous base catalyzed process, the soap formed being surface

active and interferes the separation of glycerol layer from methyl ester layer in the former case.

The solid super acids i.e. modified zirconia, titania, and heteropolyacids loaded on suitable supports are initially studied to catalyze the process of transesterification of vegetable oils for biodiesel synthesis [25]. Most of the study conducted on heterogeneous catalyzed transesterification used solid super acids since these are explored widely for their use in the refineries. The solid acid catalyzed processes require high reaction temperature i.e. more than 200 °C and high vapor pressure of methanol developed at the high temperature where the selectivity of the product is also a concern. The advantage of solid acids for biodiesel synthesis is that esterification of FFA and transesterification of triglyceride occur simultaneously. Also the solid acids are less sensitive to moisture with no side saponification reaction. The use of solid acid catalysts for biodiesel synthesis from Jatropha oil has been reported by Sun et al. [26]. The solid acids $ZrO_2–SO_4^{2-}$ and $K_4Zn_4[Fe(CN)_6]_3$ were used for esterification/transesterification of Jatropha oils with different levels of FFA and the product was analyzed by GC–MS. It is reported that the catalytic activity changed with the acid value of the oil and the reaction temperature. The methanolysis of Jatropha oil with $ZrO_2–SO_4^{2-}$ as a catalyst revealed that with the increase in FFA level of the feedstock, the catalyst loses its activity reducing the methyl ester yield up to 84%. Similar results are reported by Yee et al. [27,28]. The $K_4Zn_4[Fe(CN)_6]_3$ catalyst showed good activity and stability where methyl ester yield was 93%. The repeated use of the catalyst for five times revealed that the catalyst retains its activity towards Jatropha oil methanolysis and resulted in the methyl ester yield above 90%.

The use of base catalyst for biodiesel synthesis has recently been investigated where the vegetable oil transesterification was studied at conventional reaction conditions and at ambient pressure. Metal salts such as $CaCO_3$ and K_2CO_3 are used as catalyst for transesterification of vegetable oils. The preparation of biodiesel has been studied by potassium carbonate (unsupported) catalyzed transesterification of Jatropha oil having FFA 2.86% [29]. The mole conversion of Jatropha oil was 98.2% under the reaction conditions of 6:1 M ratio of methanol to oil, catalyst concentration 2%, and reaction temperature of 60 °C with stirring at 600 rpm for 10 h. The acid value of the product was 0.54 mgKOH/g, which is marginally higher than the specified limit. The catalytic activities of solid catalysts are further improved by impregnating on a suitable support so that the surface area is increased where the reaction occurs and active sites for the reaction are well exposed to the reactants. Potassium carbonate has been supported on Mg—Al hydrotalcite (Mg—Al ratio 3:1), calcined at 600 °C and used for transesterification of Jatropha oil [30]. 50% K_2CO_3 loaded on hydrotalcite revealed excellent morphology and particle size distribution. Upon calcinations, the catalyst K_2CO_3/hydrotalcite is forming multiple metal oxides. Under the optimized reaction conditions, the yield of biodiesel was reported to be 96%. The catalyst was reused for five times for transesterification of Jatropha oil where the catalytic activity changed negligibly with resulting biodiesel yield more than 92%.

Alkali metal supported on high surface area supports such as silica and alumina are used as solid base catalyst. The use of KNO_3/Al_2O_3 and Na/SiO_2 has recently been reported in the literature [31,32] to catalyze transesterification of Jatropha oil for biodiesel production. Alumina loaded with potassium nitrate followed by calcinations was active solid base catalyst for biodiesel synthesis from Jatropha oil. Vyas et al. [31] have synthesized the catalyst by loading 35% KNO_3 on alumina followed by calcinations at 500 °C. A conversion of 84% was obtained under the reaction conditions of 60 °C, methanol/oil molar ratio 12:1, catalyst concentration 1.5% and stirring at 600 rpm for 6 h. The kinetics of the process was investigated. The low activation energy indicated the overall reaction is less sensitive to temperature. The catalyst was recovered after the reaction and the reusability study indicated that the Jatropha oil conversion decreased to 75% during the second run and to 72% during the third run. In another study [33], the same catalyst has been reported to achieve 91.5% conversion of Jatropha oil using methanol to oil molar ratio 15:1 and reaction temperature 65 °C for 8 h, where the Jatropha oil was pretreated by the two step process prior to KNO_3/Al_2O_3 catalyzed transesterification. The regeneration of the catalyst and the reusability had also been investigated. It is needed to further improve the process for complete reaction. The aluminum modified Mg–Zn heterogeneous base catalyst has been reported [34] to catalyze the methanolysis of Jatropha oil at moderate reaction conditions. The catalyst is selective for the preparation of methyl ester from Jatropha oil containing 7.23% FFA and 3.28% water.

The use of ultrasound is well known to facilitate the reaction rate for the cases where the reactants and catalyst form different phases. To overcome the mass transfer limitation, the reactions are usually conducted at high temperature or high speed of stirring. Kumar et al. [32] studied the ultrasonic assisted transesterification of Jatropha oil catalyzed by Na/SiO_2 as mesoporous solid catalyst and achieved 98.53% conversion of biodiesel in 15 min. The activity of the catalyst was retained during three time reuse for biodiesel synthesis.

The solid calcium oxide has been investigated to catalyze the process of transesterification of vegetable oils. Zhu and co-workers [35] have prepared solid super base of calcium oxide by dipping in ammonium carbonate solution followed by calcinations at 850 °C. Under the optimum reaction conditions of methanol to oil molar ratio 9:1, catalyst concentration 1.5%, reaction temperature of 70 °C for 2.5 h, the conversion of Jatropha oil was 93%. The catalyst showed conversion of 92% Jatropha oil when the reaction was conducted with the reused catalyst. The removal of calcium from biodiesel was investigated. The viscosity of the product exceeded the specified limit. The calcium based mixed oxides have been synthesized to catalyze methanolysis of Jatropha oil [36]. The conversion of *Jatropha curcas* oil observed was above 80%. Another study [37] reported the use of lithium impregnated calcium oxide as nanocatalyst for the synthesis of biodiesel under normal reaction condition to achieve complete reaction with 99% methyl ester content in biodiesel. It needs further development of calcium oxide based catalyst for vegetable oil methanolysis to produce biodiesel satisfying the norms for fuel qualities.

Among the heterogeneous catalysts, zeolites have high surface area and large pore diameter, which allows the reactant molecules to enter into their cavity for the reaction to occur. Zeolites are flexible and versatile materials, whose acidity and/or basicity can be modulated by appropriate doping materials. Payawan et al. [9] reported the conversion of Jatropha oil using three types of solid catalysts such as amino-functionalized zeolite-Y, amino-functionalized MCM-41, and 1,5,7-triazabicyclo[4,4,0]dec-5-ene (TBD) functionalized MCM-41. The reactions were conducted with 10% catalyst loading and methanol to oil molar ratio 15:1 at 80 °C for 2 h. The yield of biodiesel was below 87% using the above mentioned catalysts. The crude Jatropha oil having acid value 107 mgKOH/g was refined prior to solid base catalyzed transesterification. The basicity of zeolites can be modulated by exchange of alkali metal ions and occlusion of alkali metal oxides in the zeolite cages by decomposition. Xue et al. [38] have developed a method to prepare artificial zeolite for biodiesel synthesis from Jatropha oil. The zeolite invented is cheap and can be used after impregnation with potassium acetate followed by drying and calcinations, which may be used to catalyze transesterification of vegetable oils. The CH_3COOK supported on artificial zeolite under optimized reaction conditions of transesterification of Jatropha oil resulted in 94.27% yield of biodiesel and the methyl ester content was 91.58%.

The use of heterogeneous catalyst for biodiesel synthesis from vegetable oil have the advantage of no soap formation, ease of separation and reuse of catalyst, environment friendly, while the process have some limitations. The international specifications of biodiesel reveal that the methyl ester content in the biodiesel should be more than 96.5% as an indication for complete conversion of oil to biodiesel and also to ascertain the fuel quality of biodiesel. The product of heterogeneous catalyzed transesterification rarely meets the requirement of methyl ester content not less than 96.5%. Further improvement in the catalyst development will improve the extent of conversion of vegetable oil to methyl esters economically to meet all the quality parameters specified in biodiesel specifications.

3.1.3. Biodiesel production using enzyme (lipase) as catalyst

In case of conventional alkali catalyzed transesterification or solid base catalyzed process, the free fatty acids is needed to be removed by pretreatment prior to the reaction. The recovery of used catalyst and glycerol is a complex process and the biodiesel product needs washing to remove impurities, i.e. soap formed during alkali-catalyzed route which contributes to additional processing cost. The above difficulties may be overcome by the use of enzyme (lipase) as biocatalyst for biodiesel synthesis from vegetable oils. Lipases catalyze the esterification of free fatty acids and transesterification of glycerides to form methyl esters. The FFA has no negative effect on transesterification of vegetable oils. The lipases are linked to insoluble matrices for immobilization to impart stability to the reaction. Immobilized lipases are explored to less extent for the use in industrial scale biodiesel production unit since the lipases are more expensive than the conventional chemical catalysts. The limitations associated with the enzyme catalyzed process are easy deactivation of lipases, low reaction rate and low conversion [18]. Various polar substances such as water, methanol, glycerol and phospholipids inhibit the catalytic activity of the lipase. In order to overcome the above difficulties, the lipase catalyzed alcoholysis may be accomplished by stepwise addition of methanol in order to minimize enzyme inactivation and also the use of organic solvent to increase the solubility of the reactants. Devanesan and co-workers [39] studied the methanolysis of Jatropha oil having acid value 17.25 mgKOH/g (FFA 8.6%) catalyzed by immobilized lipase from *Pseudomonas fluorescens* using *n*-hexane to enhance the solubility of the reactants and investigated the effect of variable parameters such as effect of temperature, pH, oil to alcohol molar ratio and reaction time. A maximum yield of 72% was achieved at optimum reaction conditions of methanol to oil molar ratio 4:1, pH 7.0 and reaction temperature 40 °C for 48 h. The reaction is not completed to desired extent so as to use the product as biodiesel. The transesterification of Jatropha oil in *t*-butanol medium using immobilized lipase from *Enterobacter aerogene* has been reported in the literature [40]. The maximum yield of biodiesel was 94% with methanol to oil molar ratio 4:1 and *t*-butanol to oil volume ratio 0.8:1 at a reaction temperature of 55 °C for 48 h. It has been observed that the presence of *t*-butanol significantly reduces the enzyme inhibition caused by methanol and glycerol. The lipase was repeatedly used for seven times until a negligible loss in the catalytic activity of lipase was observed.

In order to produce biodiesel economically from Jatropha oil, the use of immobilized whole cell biocatalyst has been investigated. The biocatalyst was prepared by immobilizing the lipase-producing whole cells of *Rhizopus oryzae* on biomass support particles [41]. The catalytic activity of this biocatalyst was compared with the most efficient lipase Novozym-435 (immobilized lipase from *Candida antarctica*) towards transesterification of Jatropha oil. The maximum methyl ester content in the reaction mixture reaches 90% after 60 h with the above biocatalyst, whereas it is 76% after 90 h when using Novozym-435. The reuse of both the enzyme for five times revealed that these lipases retain 90% of their catalytic activity. Methanolysis of Jatropha oil was observed to progress faster than other alcoholysis regardless of the lipase used.

Another way to overcome the enzyme inhibition in solvent free medium is the use of higher alcohols in place of methanol during transesterification. Shah and Gupta [42] have reported the synthesis of ethyl ester from Jatropha oil having 2.71% FFA, by the use of immobilized lipases from *Candida rugosa*, *Pseudononas cepacia*, *Pseudomonas flourescens* and *Mucor javanicus*. The process optimization for ethanolysis of Jatropha oil was studied with screening of lipases and varying reaction temperatures, percentages of enzyme used, pH and water content of the reaction medium. The immobilized lipase from *Pseudomonas cepacia* was efficient for ethanolysis to achieve a yield of 98% at reaction temperature 50 °C for 8 h in presence of 4–5% water. The enzyme was reused for four times with negligible loss in the catalytic activity of the lipase. The lipases retain their catalytic activities by the use of *iso*-propanol in place of methanol or ethanol during transesterification of triglyceride oils. The alcoholysis of crude Jatropha oil with *iso*-propanol has been studied using Novozym-435 lipase under the reaction conditions of alcohol to oil molar ratio 4:1, immobilized lipase 10% and reaction temperature of 50 °C for 8 h [43]. The maximum conversion of 92.8% was obtained using *iso*-propanol as alcohol. During repeated use for 12 cycles, the lipase retains its catalytic activity when using *iso*-propanol in the reaction whereas the catalytic activity ceased in 7 cycles during methanolysis. This indicates no negative effect on the activity of lipase when using higher alcohol such as *iso*-propanol for vegetable oil transesterification. The fatty acid *iso*-propyl ester has improved cold flow properties such as cloud point, pour point, cold filter plugging point (CFPP) and low temperature filterability test (LTFT).

The stability of immobilized lipase can be retained during the conversion of vegetable oil to biodiesel by replacing methanol/ethanol with alkyl acetates. The use of ethyl acetate as acyl acceptor for the conversion of Jatropha oil (i.e. interesterification) gives rise to fatty acid ethyl ester as product and triacetin as a by-product in place of glycerol [44]. Ethyl acetate acts as solvent as well as reactant in the lipase catalyzed interesterification so that the reaction proceeds without any negative effect on catalytic activity of the lipase. A maximum yield of 91.3% ethyl ester of Jatropha oil was achieved with the reaction conditions of ethyl acetate to oil molar ratio 11:1 and 10% Novozym-435 as a catalyst at reaction temperature of 50 °C for 12 h. The reusability of the lipase has been investigated over repeated cycles of interesterification and ethanolysis. For 12 times repeated use, the lipase retains its catalytic activity during interesterification of Jatropha oil with ethyl acetate whereas enzymatic activity reached to zero after 6th cycle for the process of ethanolysis. The enzymatic process for biodiesel synthesis is feasible by the use of immobilized lipase and higher alcohols as acyl acceptor. The high cost of enzyme is the major hurdle for commercial production of biodiesel by lipase catalyzed route.

3.1.4. Biodiesel production in supercritical fluid medium

The homogeneous alkali-catalyzed alcoholysis of vegetable oil have the limitation that the raw material needs pretreatment to have low FFA prior to transesterification so as to avoid the difficulties of formation of unwanted soap that cause difficulties for completion of the reaction and easy separation of glycerol. The separation of used catalyst needs further processing which needs extra cost to the product biodiesel. The use of heterogeneous catalyst and enzyme for synthesis of biodiesel are associated with incompleteness of the reaction to achieve methyl ester content

specified in the biodiesel specifications. The heterogeneous catalyst and enzyme catalyst need to be regenerated in order to retain their activity. The above complexities may be eliminated by conducting the alcoholysis without using the catalyst in supercritical fluid medium. The supercritical state of a material is obtained at above the critical temperature (Tc) and critical pressure (Pc) for example methanol (Tc 239.6 °C, Pc 8.09 MPa), ethanol (Tc 241.0 °C, Pc 6.14 MPa), dimethyl carbonate (Tc 274.9 °C, Pc 4.63 MPa), carbon dioxide (Tc 31.1 °C, Pc 7.39 MPa) and water (Tc 374.1 °C, Pc 22.1 MPa). The non-catalytic alcoholysis of vegetable oil with methanol in supercritical fluid medium is an alternative technology for biodiesel production where the reaction is fast and complete conversion is obtained in lesser reaction time. The reactants i.e. oil and alcohol form single phase in the supercritical alcohol mediated transesterification of oil. Under the supercritical state, the solubility parameter of methanol reduces and is close to the solubility parameter of the oil. Simultaneous esterification of FFA and transesterification of glycerides occur under supercritical state of methanol. Thus, the high FFA containing feedstock can be converted to biodiesel without pretreatment. The conversion of Jatropha oil to biodiesel under supercritical methanol has been studied [45] at 320 °C and 8.4 MPa using methanol to oil molar ratio 43:1. The Jatropha oil used in the study was extracted from seed using hexane and has FFA 2%. The completion of the reaction is achieved in 4 min. Rathore and Madras [46] reported the synthesis of biodiesel from Jatropha oil under supercritical state of methanol and ethanol without using any catalyst at reaction temperature 200–400 °C and pressure 20 MPa and the variable affecting transesterification such as alcohol to oil molar ratio, temperature and reaction time were investigated. With alcohol to oil molar ratio 50:1, the conversion is completed in 40 min. The conversion in case of supercritical ethanol is more than supercritical methanol.

The conversion of crude Jatropha oil has been studied at subcritical and supercritical methanol using micro-NaOH as a catalyst so as to conduct the reaction at mild reaction conditions. The methyl ester yield reached to 90.5% in 28 min with the reaction conditions of 0.8% NaOH, 261 °C and 7 MPa and methanol to oil molar ratio 24:1 [47]. The synthesis of biodiesel from crude Jatropha oil may also be feasible by the two step process consisting of hydrolysis of vegetable oil to fatty acids followed by esterification of FFA with methanol. Ilham and Saka [48] reported the non-catalytic conversion of crude Jatropha oil by the use of two step process. The first step is the hydrolysis of Jatropha oil under subcritical water at 270 °C and 27 MPa for 25 min to produce fatty acid and glycerol. The same process is adopted for fat splitting for fatty acid fractionation in oleochemical industries. The esterification of fatty acid is conducted in supercritical dimethyl carbonate medium in the second step. To make the process more efficient, the extraction of Jatropha oil from seed as well as the alcoholysis of oil may be conducted in supercritical state. Chen et al. [49,50] conducted the reaction of oil from seed and kernel using supercritical carbon dioxide followed by subcritical water hydrolysis of oil and supercritical methylation of hydrolyzed oil. The methyl ester content of the product was 98.5% for the process of synthesis of biodiesel from Jatropha kernel. The supercritical carbon dioxide extraction process presented maximum extraction efficiency, i.e. 94% than that of conventional cold pressing or steam pressing process of Jatropha oil which is 70% efficient. The hydrolysis of oil is followed by esterification of fatty acids to their corresponding methyl ester under dimethyl carbonate at 300 °C and 9 MPa for 10 min. The esterification of fatty acid in supercritical dimethyl carbonate is supposed to proceed by the pathway where fatty acids react with dimethyl carbonate to produce fatty acid methyl ester, glyoxal and water. The process is capable for converting high FFA Jatropha oil to biodiesel without the use of catalyst to achieve complete conversion to obtain 97% methyl ester, so as to satisfy the fuel qualities of biodiesel.

3.1.5. *In Situ biodiesel production from Jatropha oilseed*

The conventional method for producing biodiesel from oilseed involves the extraction of oil followed by its refining processes such as bleaching, degumming, dewaxing, deacidification and dehydration prior to esterification and transesterification. The oil is extracted from the oilseed either by solvent extraction or by mechanical expeller. The mechanical expeller is capable of extracting about 70% of oil present in the oilseeds. The use of organic solvent i.e. *n*-hexane is efficient to extract the oil from oilseed, which adds extra cost for organic solvent and the processing. In-situ reactive extraction for biodiesel synthesis is a new approach to eliminate the processing steps involved in the conventional process for economic production of biodiesel [51]. Shuit and co-workers [52] reported the in-situ oil extraction, esterification and transesterification for the synthesis of biodiesel from Jatropha seeds. The optimum biodiesel yield of 98.1% was achieved under the reaction conditions of temperature 60 °C, methanol to seed ratio 10.5 ml/g, catalyst concentration 21.8% H_2SO_4 and a reaction time of 10 h. The parameters investigated with the most significant effect on the yield of methyl ester in descending order is catalyst H_2SO_4 concentration followed by reaction temperature, reaction time and then methanol to seed ratio. The in situ transesterification under optimized reaction condition complete in 20–30 min [53]. The use of *n*-hexane as co-solvent improves the process [54] where the oil extraction efficiency is 91.8% and methyl ester yield is 99.8% under comparably mild reaction conditions. The use of liquid catalyst is associated with environmental disposal problem and corrosion of reaction vessels and thus the use of H_2SO_4 as a catalyst for biodiesel production in industrial scale has attracted less attention.

The use of alkyl acetates for extraction of oil from Jatropha seed and esterification/transesterification of oil is accomplished in a single step using lipase as a catalyst [55,56] without negative effect on lipase activity and to retain its operational stability. Methyl acetate and ethyl acetate act as solvents for oil extraction as well as acyl acceptors. Su et al. [55] reported in-situ synthesis of methyl and ethyl esters from Jatropha oil using respectively methyl acetate and ethyl acetate as solvents as well as acyl acceptors. Compared to the conventional two step process, the in-situ method results in high yield of ester; the improvement varies from 5.3% to 22%. The effect of solvent to seed ratio and water content on the in-situ reactive extraction was investigated. Under the optimized reaction condition, the maximum yield of 86.1% methyl ester and 87.2% ethyl ester was obtained.

Dialkyl carbonate may also be used as extraction solvent as well as transesterification reagent for in-situ lipase catalyzed reactive extraction of oilseed for biodiesel synthesis with improved conversion to alkyl esters. Su et al. [56] have developed the technique for utilizing dimethyl/diethyl carbonate for in-situ reactive extraction catalyzed by lipase Novozym-435 for synthesis of methyl/ethyl ester. The maximum yield of Jatropha methyl and ethyl ester achieved was 95.9% and 94.5% respectively.

The in-situ oil extraction and alcoholysis can also be feasible under supercritical state of alcohols. The reactive extraction of Jatropha seed is reported by Lim et al. [57], where simultaneous oil extraction as well as esterification/transesterification was accomplished in supercritical methanol with the use of *n*-hexane as a co-solvent. Under the reaction conditions of temperature 300 °C, pressure 240 MPa, methanol to Jatropha seed ratio 10 ml/g and *n*-hexane to seed ratio 2.5 ml/g, the optimum oil extraction efficiency reached up to 105.3% and methyl ester yield up to

103.5% calculated based on conventional *n*-hexane Soxhlet extraction of Jatropha oil from seed.

3.1.6. Other methods for biodiesel synthesis from Jatropha oil

The crude Jatropha oil after extraction contains polar compounds such as, FFA, water, phospholipids etc., which affect the process of alkali-transesterification. Thus, the polar compounds need separation from Jatropha oil prior to transesterification. A new method was developed where the solvent for oil extraction is a two-phase system consisting of n-hexane and methanol [58]. The conditions for oil extraction from 30 g sample requires 240 ml extraction solvent mixture, temperature 35 °C and time 30 min. On increasing the methanol volume from 0% to 60% in the extraction solvent, the oil extraction efficiency remains mostly unchanged, but the FFA content in the oil reduced from 5.27 to 0.42 and similarly water content reduced from 2.268 to 0.046. The FFA and water content in the extracted oil met the requirement for alkali-catalyzed transesterification. After two phase solvent extraction, the oil containing *n*-hexane was subjected to transesterification with methanol. The *n*-hexane from the oil extraction step acts as a co-solvent for the reactants. Under the optimized condition of transesterification for the synthesis of biodiesel, a conversion of 98% was achieved. The product biodiesel obtained after two phase extraction and transesterification met ASTM specifications for biodiesel.

The approach for enzymatic splitting of vegetable oils to fatty acids and subsequently simple acid catalyzed fatty acid esterification step has also been investigated. de Sausa et al. [59] recovered the lipase from germination of Jatropha seed and utilized for hydrolysis of Jatropha oil. The experimental results revealed 97% conversion of oil to fatty acid. The methyl esterification of fatty acid was accomplished by the use of heterogeneous acid catalyst resulting in 97.1% methyl ester in biodiesel.

A method has been developed by Budiman et al. [60] for continuous production of biodiesel from Jatropha oil to make the process efficient and cost effective. A continuous reactive distillation process integrates the feature of reaction and separation of the product in one unit. This process has the advantage for completeness of the reaction. Synthesis of biodiesel from refined Jatropha oil has been studied by the continuous reactive distillation process with methanol to oil molar ratio 10:1 and 0.75% NaOH as a catalyst, at the reaction temperature 65 °C. The conversion of Jatropha oil to biodiesel was 94.83% and the methyl ester content was 99.27%, the fuel characteristics met the ASTM biodiesel specification.

3.2. Comparison of existing biodiesel production technologies

The biodiesel production technologies are described in detail in the previous section. The homogeneous alkali catalyzed route is the conventional method for complete conversion of vegetable oils to obtain biodiesel having fuel quality as per EN 14214, ASTM 6751 and IS 15607 norms. The alkali catalyzed process requires mild reaction conditions i.e. reaction temperature 60–65 °C at ambient pressure and short reaction time. The limitation of the alkali catalyzed process is the requirement of the pretreatment step for the feedstock containing high free fatty acids and the recovery of the used catalyst is commercially not feasible. In order to avoid the pretreatment steps, the research and development on biodiesel has focused on the other methods such as heterogeneous catalytic route, enzymatic method and supercritical methanol process.

The heterogeneous catalytic route for biodiesel production is capable of converting the high FFA oils to biodiesel and the catalyst is recovered and re-used for repeated times. The limitation of the process is the requirement of severe reaction conditions i.e. high reaction temperature or high ratio of methanol to oil, long reaction time and incompleteness of the reaction to desired extent to obtain methyl ester content more than 96.5% [61,62]. The enzymatic route of biodiesel synthesis does not require reducing the FFA level in the vegetable oil and the free fatty acids are also converted to methyl esters. The enzymes can be recovered and reused for repeated times. The limitation of the enzymatic process is the longer reaction time and the high cost of enzyme to make biodiesel economically feasible. The biodiesel production technology in supercritical methanol is an efficient process where the reaction does not require any catalyst, is completed in few minutes and free fatty acids has no negative influence on the process. The limitation of the supercritical methanol process is the severe reaction condition having safety concern and requires more infrastructures for industrial scale biodiesel production.

3.3. Industrial scale biodiesel production

Commercial biodiesel production units use homogeneous alkali catalyzed process for efficient and cost effective production of biodiesel to meet the fuel qualities. Among the homogeneous alkali catalytic process, metal alkoxides result in higher selectivity of the product [16]. The transesterification of vegetable oils catalyzed by methoxide of sodium or potassium requires low reaction temperature 60–65 °C at ambient pressure, the reaction is completed in one hour. The methoxide catalyzed process results in complete conversion of the triglyceride oil to fatty acid methyl esters so that the produced biodiesel attains the methyl ester content > 96.5% and the free glycerol and total glycerol within the limits specified by EN 14214, ASTM 6751 and IS 15607 biodiesel specifications. The completeness of the reaction is essential for attaining the biodiesel specifications. The sodium hydroxide or potassium hydroxides are used as catalysts for vegetable oil transesterification; the catalytically active species is the methoxide ion which is generated by dissolution of hydroxides in methanol. The formation of methoxide by the reaction of methanol with hydroxide is represented in scheme (a) of Fig. 1, and the same is associated with formation of a molecule of water. The presence of water molecule during vegetable oil transesterification decreases the selectivity of the product. The feedstock triglyceride or the end product methyl esters undergo saponification in the presence of catalyst sodium hydroxide and water and the reaction is irreversible. The saponification of triglyceride or methyl ester is described in scheme (b) of Fig. 1. The soap formed during transesterification has a negative effect on completion of reaction and glycerol

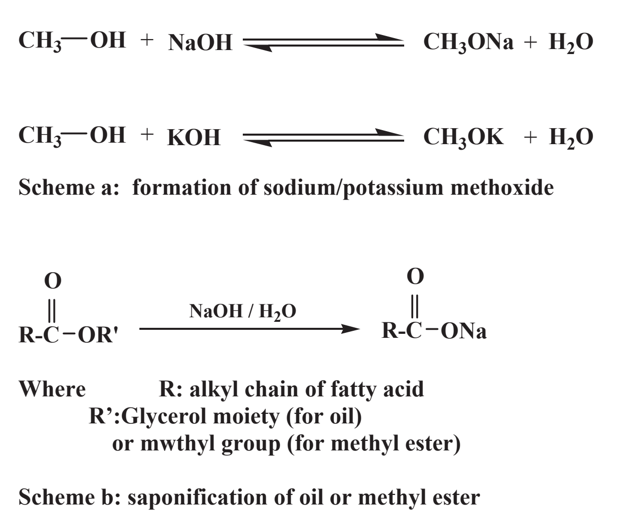


Fig. 1. Formation of sodium or potassium methoxide (Scheme a) and saponification of oil or biodiesel (Scheme b).

separation. Also the dissolution of hydroxide in methanol is an exothermic process which is a concern for safety. The above difficulties are eliminated by the use of sodium methoxide 25–30% in methanol or potassium methoxide 32% in methanol, which are commercially available for biodiesel synthesis. 30% solution of sodium methoxide in methanol is a cheap catalyst for the production of biodiesel with the reduced risk of handling in industrial scale units.

The feedstock vegetable oil for the sodium methoxide catalyzed process needs to have free fatty acid less than 0.1%, moisture less than 0.1%, phosphorus content less than 10 ppm and unsaponifiable matter less than 0.8% as specified by biodiesel manufacturers such as Lurgi [63] and Desmet Ballestra [64]. The same specification of feedstock Jatropha oil may be achieved by the process of pretreatment steps. The pretreated feedstock of the above specification and methanol and catalyst sodium methoxide solution are fed to the continuous reaction vessels. The transesterification units are designed in such a way that the reaction is accomplished in two or three steps and in between, the produced glycerol rich layer are removed, so that the reaction proceeds towards completion in 2—3 h residence of the reactants. After completion of transesterification, the glycerol is separated and the biodiesel layer is subjected to methanol recovery and distillation, neutralization of residual catalyst in biodiesel, and washing and drying of biodiesel.

4. Characteristics of Jatropha based biodiesel

The fuel qualities of biodiesel derived from Jatropha oil has been investigated by various researchers [4,14,15,24,32,48] and the results are listed in Table 4. Most of the fuel characteristics as listed in biodiesel specifications are dependent on the extent of completion of the reaction as well as post-transesterification processes and these qualities meet the biodiesel specification. The fuel qualities namely linolenic acid methyl ester, polyunsaturated methyl ester, iodine value, oxidation stability and cold flow properties such as cloud point, pour point, CFPP and low temperature filterability test (LTFT) are dependent on the chemical composition of the feedstock. The Jatropha methyl ester meets all requirements for American, European and Indian specifications except the oxidation stability. The EN 14214 and IS 15607 specify the minimum induction time of 6 h for determining the oxidation stability of biodiesel at 110 °C with 10 L/h air flow using the Rancimat method EN 14112. The induction period of Jatropha based biodiesel is shown in Table 4. The lower oxidation stability of Jatropha based biodiesel is because of higher percentage of poly-unsaturated fatty acid present in the oil which are susceptible for faster oxidation. The oleochemical containing at least one double bond in the hydrocarbon chain means there is always atleast one allylic position that is prone to give up a hydrogen atom and form a stable allylic radical as depicted in Fig. 2. With time, oxygen removes an allylic hydrogen to form an allylic radical, which in turn produces hydroperoxides and related products. It is the taste and odor of the compounds especially the carboxylic acids that are associated with the spoilage or rancidity of such fatty acid derivatives. A well known example of autoxidation occurs with fatty acid i.e. linoleic acid having two double bonds (at C-9 and C-12) making the methylene group at C-11 doubly allylic and very susceptible for autoxidation [65]. The relative rates of oxidation given in the literature are 1 for oleates (methyl, ethyl esters), 41 for linoleates and 98 for linolenates [66,67].

The oxidation stability of Jatropha methyl ester has been improved by blending it with biodiesel rich in saturated fatty acid methyl ester such Palm biodiesel. It has been observed that 60% Palm based biodiesel is needed to meet the requirement of Rancimat induction period of 6 h [15]. The oxidation stability of biodiesel is also affected by contamination with metals when stored in a metallic container or storage tank. The oxidation stability of Jatropha based biodiesel can be improved by the use of free radical scavengers. In order to improve the oxidation stability of biodiesel, the effects of natural and synthetic antioxidants have been investigated [68]. The study revealed that the synthetic antioxidants are effective in improving the oxidation

Table 4
Fuel quality of Jatropha methyl ester.

Sl. no.	Properties	Ref. [4]	Ref. [14]	Ref. [48]	Ref. [15]	Ref. [32]	Ref. [24]
1.	Density @15 °C, kg/m^3	884.2	879.0	–	–	887.3	880.0
2.	Kinematic viscosity at 40 °C, cSt	4.4	4.8	4.5	4.4	4.28	4.8
3.	Flash point, °C	172	191	–	163	134	–
4.	Sulfur, ppm	–	–	–	30	100	–
5.	Carbon residue, % by mass	–	0.02	0.15	< 0.01	–	–
6.	Sulfated ash, % by mass	–	0.014	n.d.	0.002	–	–
7.	Water content, ppm	590	1600	302	500	236	–
8.	Total contamination, ppm	2	–	–	–	–	–
9.	Copper corrosion, 3 h at 50 °C	1	–	–	1	1	–
10.	Cetane number	58.5	51	–	57.1	53	–
11.	Acid value, mgKOH/g	0.11	0.24	0.1	0.48	0.22	0.38
12.	Methanol, % by mass	< 0.02	0.06	–	–	–	–
13.	Ester content, % by mass	98.9	99.6	97.2	–	–	99.56
14.	Linolenic acid methyl ester, % by mass	–	–	–	–	–	0
15.	Polyunsaturated (≥ 4 double bonds) methyl esters, % mass	–	–	–	–	–	0
16.	Monoglyceride, % by mass	0.01	0.24	0.2	–	0.08	0.5
17.	Diglyceride, % by mass	0.02	0.07	0.07	–	0.06	0.12
18.	Triglyceride, % by mass	< 0.02	0	0	–	0.06	0.1
19.	Free glycerol, % by mass	< 0.02	0.015	–	0.01	–	0.02
20.	Total glycerol, % by mass	0.03	0.088	0.08	0.02	–	0.07
21.	Phosphorus, ppm	< 1	17.5	–	< 10	–	–
22.	Sodium and Potassium, ppm	< 1	–	–	–	–	–
23.	Calcium and Magnesium, ppm	< 1	7.5	–	–	–	–
24.	Iodine value, gI_2/100 g	93	–	100	–	–	–
25.	Oxidation stability at 110 °C, h	6.7	–	3.3	3.23	3.5	–
26.	Cloud point, °C	–	–	−3.0	4.0	–	–
27.	Distillation T90 AET, °C	–	–	–	–	–	–

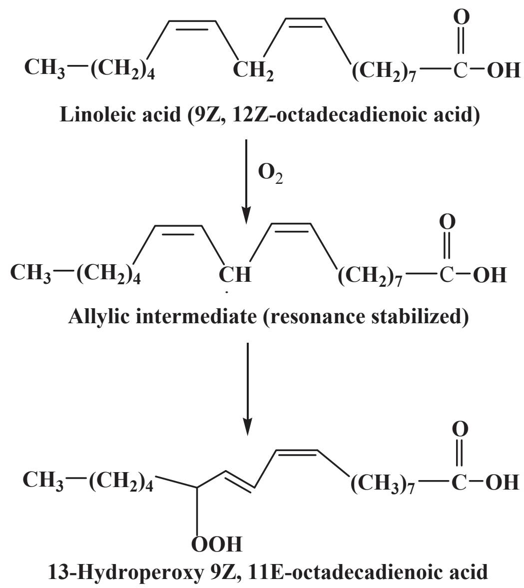


Fig. 2. Autoxidation of linoleic acid.

stability of jatropha based biodiesel. Attempts have been made to improve the oxidation stability by the use of synthetic antioxidants [69,70] and the use of metal deactivator in combination with antioxidant for metal contaminated biodiesel. The synthetic antioxidants i.e. pyrogallol (PY), propylgallate (PG), *tert*-butylhydroxyquinone (TBHQ), 3-*tert*-butyl-4-hydroxyanisole (BHA) and 2,6-di-*tert*-butyl-4-methyl-phenol (BHT) when added to biodiesel in ppm level have reported to enhance the oxidation stability [71,72]. The use of synthetic antioxidant for improving the oxidation stability of Jatropha methyl ester is cost effective to enable the fuel to meet the requirement of ASTM 6751, EN 14214 and IS 15607 specifications.

5. Future aspects

The technology for vegetable oil conversion to biodiesel has been well developed where most of the biodiesel manufacturers are utilizing edible oils as feedstock. The use of edible oil as raw material for biodiesel is creating a condition of food versus fuel, which leads to the concept of using non-edible oil as biodiesel feedstock.

The non-edible Jatropha oil may serve as raw material for the partial fulfillment of increasing demand for diesel. Initiatives have been taken in the tropical and sub-tropical countries for Jatropha cultivation to produce biodiesel. Importance must be given to other possible bio-fuel products from Jatropha cultivation which includes the generation of methane from de-oiled cake, fuel briquette from husk, the Jatropha biomass which can be used to produce syn-gas followed by Fisher—Tropsch process to obtain desired fuel, and pyrolysis of the Jatropha biomass to bio-oil having physico-chemical properties comparable to crude petroleum.

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